

CLAIMS

1. Process for preparing an electrode that is at least partly coated with a film obtained by spreading and drying, on an electrode support, an aqueous solution comprising at least one active material, at least one water soluble binder and at least one water soluble thickener.
2. Process according to claim 1, in which the active material is selected from the group consisting of:
 - a. metallic oxides;
 - b. ceramics;
 - c. carbon, natural graphite and synthetic graphite;
 - d. metals;
 - e. semi-conductor materials; and
 - f. mixtures of at least two thereof.
3. Process according to claim 2, in which:
 - a. the metallic oxide is selected from the group consisting of LiMn_2O_4 , LiCoO_2 and LiNiO_2 ;
 - b. the carbon is selected from the group consisting of high surface area carbon, graphite, carbon fibers and cokes;
 - c. the metals are selected from the group consisting of Ag, Sn, and Cu; and
 - d. the semi-conductor material is Si.
4. Process according to any one of claims 1 to 3, in which the chemically and/or electrochemically active material is in the form of powder whose average particle size is between 10 nanometers and 50 micrometers.

5. Process according to claim 4, in which the powder has a granular dispersion between 200 nanometers and 25 micrometers.
6. Process according to any one of claims 1 to 5, in which at least 20 % of the binder and/or thickener are water soluble at the rate of 20 grams in 100 grams of water, at room temperature.
7. Process according to claim 6, in which at least 50 % of the binder and/or thickener are soluble.
8. Process according to claim 7, in which at least 90 % of the binder and/or thickener are soluble.
9. Process according to claim 8, in which the water soluble thickener is selected from the group consisting of natural celluloses, modified celluloses, natural polysaccharides and modified polysaccharides.
10. Process according to claim 9, in which the soluble thickener has a molecular weight between 27,000 and 250,000.
11. Process according to claim 9 or 10, in which the thickener is selected from the group consisting of carboxymethylcelluloses, hydroxymethylcelluloses and methylethylhydroxycelluloses.
12. Process according to any one of claims 1 to 11, in which the thickener is selected from the group consisting of carboxymethylcelluloses of the type Cellogen®.
13. Process according to claim 12, in which the thickener is selected from the group consisting of EP, 7A, WSC. BS-H and 3H carboxymethylcelluloses, sold by Daiichi Kogyo Seiyaku Co. of Japan.
14. Process according to any one of claims 1 to 14, in which the binder is a natural or synthetic rubber.

15. Process according to any one of claims 1 to 14, in which the binder is of the non fluorinated type or of the low fluorinated type.
16. Process according to claim 14 or 15, in which the rubber is selected from the group consisting of SBR's, NBR's, HNBR's, CHR's and ACM's.
17. Process according to claim 15 or 16, in which the rubber is a SBR characterized in the form of a paste at room temperature.
18. Process according to claim 17, in which the STYRENE BUTADIENE RUBBER (SBR) selected is the one sold by NIPPON ZEON'S BINDER BATTERY GRADE (BM-400B) or the like.
19. Process according to any one of claims 13 to 18, in which the thickener is EP and/or 3H.
20. Process according to any one of claims 1 to 19, in which the electrode is an anode and the aqueous solution used for spreading contains by weight:
 - a. at least 64 % graphite; and
 - b. at least 3 % water soluble binder,
 - c. from 0.1 to 2% thickener; and
 - d. at most 27 % water.
21. Process according to any one of claims 1 to 19, in which the electrode is a cathode and the aqueous solution used for spreading contains by weight:
 - a. at least 64 % LiFePO_4 ; and
 - b. at least 3 % water soluble binder,
 - c. from 0.1 to 2% thickener; and
 - d. at most 27 % water.

22. Process according to any one of claims 1 to 21, in which at least 95 % of the water that is present in the spreading solution is evaporated after spreading.
23. Process according to claim 22, in which the traces of H₂O that are present at the surface of the electrode, after its coating with the aqueous solution, are removed by heat treatment in line of the EXT, DBH and/or DB process or by Infrared, preferably at a temperature between 80 and 130° Celsius for a period of time between 1 and 12 hours.
24. Process according to claim 10, in which the electrode is of the non salted type.
25. Process according to any one of claims 1 to 24, carried out in ambient air and by using the Doctor Blade extrusion method and/or the electrostatic method.
26. Process according to any one of claims 1 to 20 and 22 to 25, in which the electrode is negative and the electrochemically active material used is selected from the group consisting of powders of the graphite, alloy of Sn, of Si, Li₄Ti₅O₁₂, WO₂ types and mixtures of at least two of these components.
27. Process according to claim 26, in which the graphite powder consists of ellipsoidal shaped particles coated with prismatic shaped graphite particles.
28. Process according to claim 20, in which coating of ellipsoidal graphite with prismatic graphite is obtained by mechano-melting and/or by hybridization.
29. Process according to any one of claims 1 to 19, 21 and 22 in which the electrode is positive and the electrochemically active material is

selected from the group consisting of powders of LiCoO_2 , LiNiO_2 , $\text{Li}_2\text{Mn}_2\text{O}_4$, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, LiFePO_4 coated with graphite and carbon and mixtures of at least two thereof.

30. Process according to claim 29, in which the electrode is prepared from particles of LiFePO_4 coated with particles of graphite and/or carbon.

31. Process according to claim 30, in which the specific surface area of the carbon present in the coating, measured by BET, is $\geq 50 \text{ m}^2/\text{g}$.

32. Process according to claim 30 or 31, in which coating of LiFePO_4 with carbon and/or graphite is carried out by mechano-melting or by hybridization.

33. Electrode consisting of a support coated at least in part with a film containing one active material, said electrode being obtained by implementation of one of the processes according to any one of claims 1 to 25.

34. Electrode according to claim 33, that is a cathode in which the electrode support consists at least in part of stainless, aluminum, copper, carbon, metal-plastic or a mixture of at least two of these materials.

35. Electrode according to claim 33 that is an anode in which the electrode support consists at least in part of copper, metal-plastic, or a mixture of at least two thereof.

36. Electrode according to any one of claims 33 to 35, having at least one of the following properties:

- a. storage stability, preferably higher than 1 year, in the presence of a moisture content higher than 50 % and in the presence of temperatures higher than 20°Celsius ;

- b. a film thickness when the latter is graphite based that is between 10 and 100 μm , still more preferably between 20 and 45 μm and according to the most advantageous mode the film has a thickness of about 45 μm ;
 - c. a film thickness when the latter is iron and/or phosphate based that is between 20 and 200 μm , still more preferably between 20 and 110 μm , the most advantageous mode being the one in which the film has a thickness of about 90 μm ;
 - d. electrochemical performances that compare to those of corresponding electrodes obtained with the same active material but by using an organic solvent solution; and
 - e. an electrode film characterized by the fact that particles of rubber are directly attached to the electrode support.
37. Electrode according to claim 36, in which the porosity of the film that coats one or more of the electrodes, measured according to the method of thickness measurement, is between 10 and 90 %.
38. Electrode according to claim 37, in which the porosity is between 30 and 40 %.
39. Process for preparing an electrochemical system from its constituents including at least one anode, at least one cathode and at least one separator, in which at least one anode and/or at least one cathode has been obtained by a process described in any one of claims 1 to 32 or as defined in any one of claims 33 to 38.
40. Process according to claim 39 for the preparation of a battery in which the separator is porous.

41. Process for preparing an electrochemical battery according to claim 40, in which the separator is preferably of the PP or PE type or of the (PP,PE) mixture type.
42. Process according to any one of claims 39 to 41, in which the separator is preferably obtained by extrusion.
43. Process according to claim 39, in which the separator is of the gel type.
44. Process according to claim 41, in which the separator is obtained from polymer materials of the type:
- polyester,
 - poly(vinylidene fluoride) of chemical formula $(\text{CH}_2\text{-CF}_2)_n$, with n preferably varying between 1000 and 4000, preferably such that n is close to 150, preferably those having an average molecular weight between 10,000 and 1 million, still more preferably those having an average molecular weight between 100,000 and 250,000;
 - poly(vinylidene fluoro-co-hexafluoropropene) copolymers, of formula $[(\text{CH}_2\text{-CF}_2)_x(\text{CF}_2\text{-CF}(\text{CF}_3))_{1-x}]_n$ in which n varies from 1000 to 4000, preferably n varies from 2000 to 3000, still more preferably n is close to 150 and x preferably varies between 0.12 and 0.5, preferably those having an average molecular weight between 10,000 and 1 million, still more preferably those having an average molecular weight between 100,000 and 250,000;
 - poly(tetrafluoroethylenes), of chemical formula $(\text{CF}_2\text{-CF}_2)_n$, with n varying from 5 to 20,000, preferably n varying from 50 to 10,000, preferably those having an average molecular weight

between 500 and 5 millions, still more preferably those having an average molecular weight between 5,000 and 1,000,000, preferably about 200,000;

- poly(ethylene-co-propylene-co-5-methylene-2-norbornenes) or ethylene propylene-diene copolymers, also called EPDM, preferably those having an average molecular weight between 10,000 and 250,000, preferably between 20,000 and 100,000; and
- the poly(methylmethacrylates) also called (PMMA), of formula $[(CH_2-C(CH_3)(CO_2CH_3))_n]$, with n preferably varying between 100 and 10,000, still more preferably n varying from 500 to 5000, preferably those having an average molecular weight between 10,000 and 1 million, preferably those having an average molecular weight between 50,000 and 500,000; and
- mixtures of at least two thereof.

45.Process according to claim 44, in which the separator is of the polyether PEO-PPO copolymer type.

46.Process according to claim 44, in which the separator is of the 3 branch polyether type or of the 4 branch polymer type.

47.Process according to claim 46, in which the separator is preferably of the 4 branch polymer type manufactured by DKS Japan and sold under the trademark ELEXCEL[®] ERM1.

48.Electrochemical system that can be obtained by a process comprising at least one process step as defined in any one of claims 39 to 47.

49.Electrochemical system comprising at least one electrode obtained by implementation of a process according to any one of claims 1 to 32 or

- as defined in any one of claims 33 to 38, a separator of the gel, solid or liquid electrolyte type.
50. Electrochemical system according to claim 48 or 49, comprising an electrolyte gel.
51. System according to claim 50 of the all liquid battery type, in which the electrolyte includes at least one salt and at least one solvent.
52. System according to claim 51, in which the salt molar concentration, in the electrolyte, is lower than or equal to 1 and the solvent molar concentration is higher than or equal to 1.
53. System according to claim 51 or 52, in which the salt is preferably a salt of the imide family, of the type LiPF_6 , LiBF_4 , LiBOB , LiTFSI or LiFSI or a mixture of at least two of the latter, such as mixtures of LiBOB and LiFSI .
54. System according to any one of claims 51 to 53, in which the retained solvents have an elevated boiling point.
55. System according to claim 54, in which the solvent has a boiling point higher than 100 °Celsius.
56. System according to claim 55, in which the solvent is of the type γBL , TESA, or modified TESA, or mixtures thereof.
57. System according to any one of claims 51 to 55, in which EC and PC solvents are used for the formation of the passivation film in the case of carbon based anodes, and PC solvent for low temperature applications.
58. System according to claim 57, in which the electrolyte for the all gel battery is obtained from a precursor made of a) a polymer + b) a liquid electrolyte.

59. System according to claim 58, in which the a) content varies from 1 to 99 %, preferably this content varies from 5 to 25 %; and the b) content varies from 1 to 99 %, preferably, this content varies from 75 to 95 % and the a and b contents agree with the relation $(a) + (b) = 100 \%$, the % being given in weight.
60. System according to claim 59, in which a thermo-initiator is added in amounts that are proportional to the total weight $a) + b)$, or preferably in amounts between 100 and 5000 ppm, preferably in amounts between 500 and 1000 ppm.
61. System according to claim 60, in which the composition of the precursor is about 5 % of a 4 branch polyether preferably of the ELECEL type, and about 95 % of an electrolyte of composition $(1.5 \text{ LiTFSI} + \text{EC} + \text{PC} + \text{TESA} + \gamma\text{BL} (1 : 1 : 1 : 2))$.
62. System according to claim 61 in which, the concentration in lithium salt is higher than or equal to 1 M (1 molar) for the gels.
63. System according to claim 61, in which, the concentration in lithium salt is lower than or equal to 1 M (1 molar) in the liquid electrolyte.
64. Use of a water soluble polymer, preferably a polymer of the Styrene Butadiene Rubber type, still more preferably a SBR sold by NIPPON ZEON'S BINDER BATTERY GRADE (BM-400B) as binder in an aqueous solution for the preparation of a film for coating part or the totality of an electrode support.
65. Use according to claim 64, without any formation of HF.
66. Use according to claim 65, in which the formation of HF is avoided by using an imide salt.
67. Use according to any one of claims 64 to 66, in which the preparation of the film is carried out by cross-linking the polymer solution that

- coats the electrode by using thermal radiation after the electrode has been placed in the battery, the battery is closed and sealed.
68. Use according to claim 67, in which cross-linking of the polymer solution is preferably carried out by Infra Red.
69. Use according to claim 67 or 68, in which the polymerization temperature is between 40 and 80 °Celsius.
70. Use according to any one of claims 64 to 69, in which cross-linking of the polymer lasts between 5 minutes and 2 hours.
71. Use according to claim 70, in which the polymerization is carried out at about 80 °Celsius and during about 10 minutes.
72. Use according to any one of claims 64 to 71, in which the battery is flexible and of the multilayer metal plastic type.
73. Use according to claim 72, for reducing the weight and cost of manufacture due to the fact that it is not required to have a protective layer against HF, that is removed during the process.
74. Use according to any one of claims 64 to 73, for the preparation of super condensers preferably for the preparation of hybrid type of super condensers.
75. Use according to any one of claims 64 to 73, in which the cathode support is of the aluminum type preferably of the EXMET[®] expanded metal type.
76. Use according to any one of claims 64 to 73, in which the anode support is of the full copper type, preferably EXMET[®] or conductive metal plastic when the average voltage is lower than or equal to 1.6 Volts and the cathode support is of full aluminum, preferably EXMET[®] or conductive metal plastic when the average voltage is higher than 1.6 Volts.

77. Process for preparing an electrochemical separator at least partly coated with a polymer type film, preferably of the SBR type that is water soluble.
78. Process for preparing an electrochemical separator according to the processes of preparing electrodes defined in any one of claims 1 to 32, except that the aqueous polymer solution that is used contains no active materials nor carbon, or very small quantities thereof.
79. Electrochemical system including at least three constituents namely at least one anode, at least one cathode and at least one separator and in which at least two, and preferably at least three of the constituents of the system have been prepared by implementation of one of the processes according to any one of claims 1 to 32 and/or by implementation of a process according to claim 77 or 78.
80. Electrochemical system according to claim 79 in which the constituents have been prepared without using organic solvents.